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Anomalously soft dynamics of water in carbon nanotubes

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Abstract

The structure and dynamics of water confined to the one-dimensional nanotube interior are found to be drastically altered with respect to bulk water. Neutron diffraction, inelastic and quasielastic neutron scattering measurements in parallel with MD simulations have clearly shown the entry of water into open-ended single-wall carbon nanotubes and identified an ice-shell plus central water-chain structure. The observed extremely soft dynamics of nanotube-water arises mainly from a qualitatively large reduction in the hydrogen-bond connectivity of the water chain. Anomalously enhanced thermal motions in the water chain, modeled by a low-barrier, flattened, highly anharmonic potential well, explain the large mean-square displacement of hydrogen and the fluid-like behavior of nanotube-water at temperatures far below the nominal freezing point.
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The incorporation of water into carbon nanotubes may provide a simplified analogy to water/protons in transmembrane channels and so is of interdisciplinary scientific interest. Recently [1] we have studied quasi-one-dimensional water encapsulated inside open-ended single-wall carbon nanotubes (SWNT) of 14 Å diameter (and ~10 μm long), here referred to as *nanotube-water*, by means of neutron diffraction (ND), inelastic neutron scattering (INS) and quasielastic neutron scattering (QENS) using the SAND, HRMECS and QENS beamlines at IPNS. The entry and confinement of water molecules inside SWNT were first shown by ND [1].

The combined high incident energy (600 meV) and low scattering angles permitted the observation of the entire spectrum at relatively small momentum transfer so that damping of the intensity by the large Debye–Waller factor can be minimized. The generalized vibrational density of states, $G(E)$, obtained from INS spectra measured at 9 K (see Fig. 1A), shows a large shift to higher energies in the intramolecular stretching O–H modes for nanotube-water ($E_{str} = 422$ meV) compared to normal ice-Ih ($E_{str} = 406$ meV). The intermolecular librational band (45–115 meV) for nanotube-water is softer compared to that in ice-Ih (with an average shift of the total band by about 15–20 meV). There is no gap between the translational (below 40 meV) and librational bands in the spectrum of nanotube-water, which is a characteristic feature in INS spectra of all other previously studied bulk phases of ice (see e.g. Refs. [2,3]). The translation band shows large changes compared to ice-Ih, demonstrating a strong suppression in intensity of the high-energy optical peak around 36 meV with noticeable redistribution of intensity towards lower energies, resulting in a new peak at ~23 meV. The acoustical part of the nanotube-water spectrum (in the range 2–5 meV) shows a strong (by a factor of 2) increase of intensity compared to ice-Ih (Fig. 1B). The blue shift of the stretching modes in conjunction with the red shift of the intermolecular modes with extra spectral density extending to lower energies indicate a weakened hydrogen-bonded network in nanotube-ice.

The mean-squared displacements of hydrogen atoms in nanotube-water, $\langle u_H^2 \rangle$, obtained from high-energy-resolution QENS data ($\Delta E = 80$ μeV), show anomalously large

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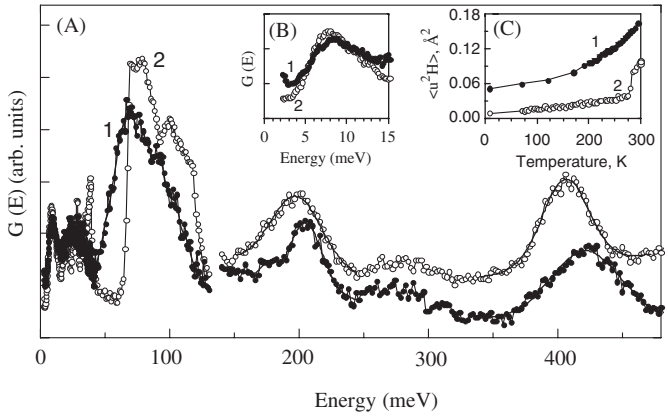

Fig. 1. (A) Vibrational spectra ($T = 9$ K) of nanotube-water and ice-Ih. Inset (B) shows the acoustical part of spectra in an enlarged energy scale. (C) Mean-squared displacement of hydrogen atoms in nanotube-water compared to ice-Ih. Curves with solid points (1) and with open points (2) are for nanotube-water and ice-Ih, respectively.

values (by a factor of ~4) compared to ice-Ih (see Fig. 1C) or any other known ice phases. Note that at 8 K the $\langle u_H^2 \rangle$ for nanotube-water already exceeds the value for ice-Ih before its melting point.

Molecular dynamics (MD) calculations for water in SWNT were performed using the TTM2-F polarizable flexible water model of Burnham and Xantheas with smeared charges and dipoles to model short-range electrostatics [4]. This model was able to accurately account for the high-level electronic structure data of water clusters and to reproduce the bulk behavior of ice and ambient liquid water. The MD water simulations were performed in a rigid (10,10) carbon nanotube of ~13.8 Å diameter and 40 Å length subjected to periodic boundary conditions and SWNT–water interactions via a Lennard-Jones potential [5]. An Ewald sum was used to incorporate the long-range Coulomb interactions.

A new structure for low-temperature nanotube-water (Fig. 2) has been proposed based on MD simulations [1]. This structure differs from the previous model [6] in that it is built up of two quite different sub-structures: (i) a 'shell' of water molecules wrapped into a cylinder-like formation parallel to the nanotube axis (shell molecules) and (ii) an interior water chain that runs through the cylindrical shell of waters (chain molecules). Previous simulations [6] have only predicted the shell molecules for a nanotube of this size. Fig. 3 shows the calculated O–O radial distribution functions (RDF) for nanotube-water, chain water and chain–shell water. Due to one-dimensional character the coordination number for the water molecules in the chain is only 1.86, which is much less than the 4- and 3.8-coordination for bulk ice and liquid water, respectively. The featureless RDF for the chain–shell indicates virtually no structural correlation between chain and shell water molecules.

Simulations using the proposed structure for nanotube-water have helped differentiate the dynamics between the chain and the shell and explain the experimentally observed

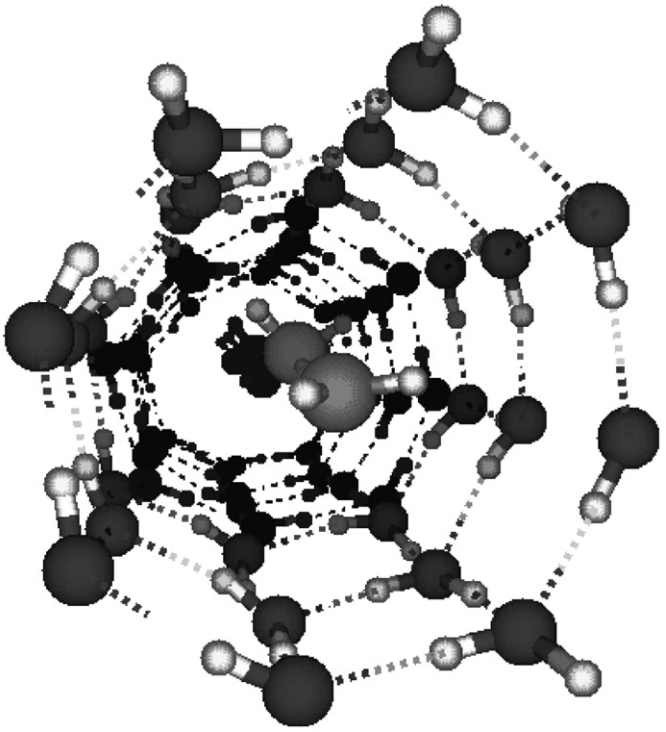

Fig. 2. Proposed structure of nanotube-water consisting of a 'shell' of water wrapped into a cylinder and an interior water chain that runs through the cylindrical shell of water.

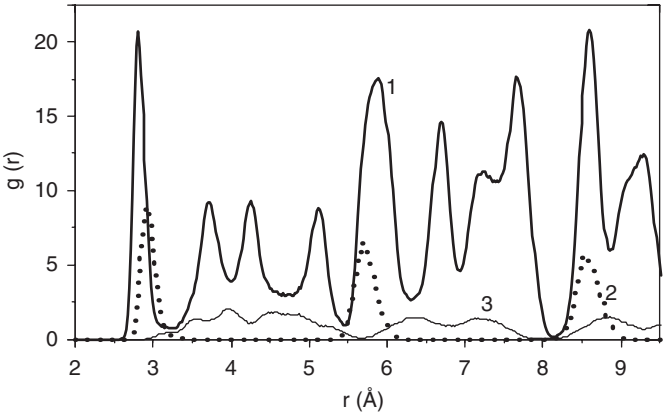

Fig. 3. Calculated O–O RDF functions for nanotube-water at 100 K. Chain molecules have an average coordination number of 1.86 – much less than that (~3.8) in the bulk liquid. (1) – shell water, (2) – chain water, (3) – chain-shell.

anomalous behavior of vibrational spectra and mean-squared displacements of hydrogen atoms. The model containing only shell water, similar to that in Ref. [6], failed to describe the experimental data (see Fig. 4). The soft dynamics of nanotube-water arises mainly from the drastic change in hydrogen-bond connectivity of the central chain water, which results in continually breaking and forming the hydrogen bonds between the neighboring water molecules in the chain and to a much greater extent between the shell–chain molecules even down to 50 K.

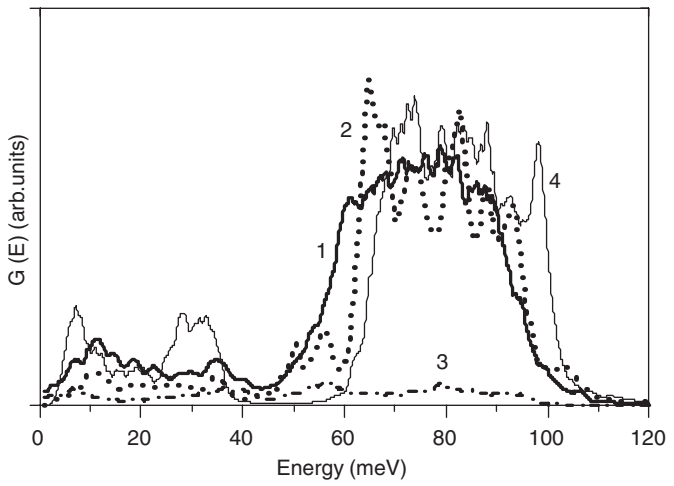

Fig. 4. *G(E)* spectra obtained from MD simulations at 50 K for nanotube-water (1), shell molecules separately (2), chain molecules (3) in nanotube-water, and ice-Ih (4).

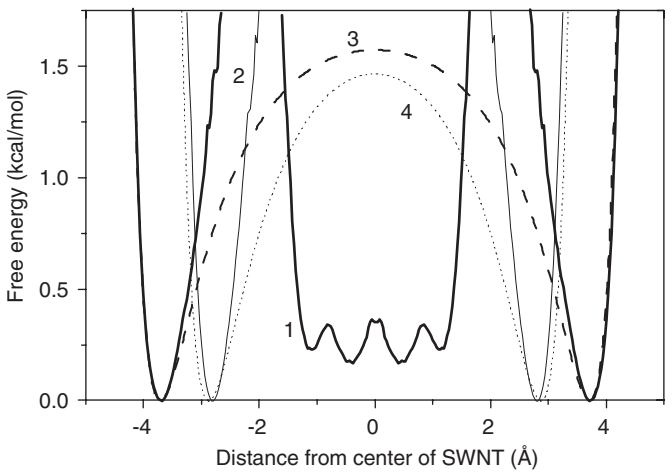

Fig. 5. Free energies across the nanotube walls for water molecules in nanotube-water at 100 K in (10,10) and (9,9) SWNTs (thick and thin solid curves 1 and 2, respectively). The L-J potential provides the minima for the position of individual water molecules initially entering the SWNT (dashed and dotted curves 3 and 4, respectively for (10,10) and (9,9) SWNT).

Anomalously enhanced thermal motions of the chain water, interpreted by a low-barrier, flattened, highly anharmonic potential well (see Fig. 5), explain the large mean-square displacement of hydrogen and the fluid-like behavior of nanotube-water at temperatures far below the nominal freezing point. This behavior resembles qualitatively the expected soft dynamics associated with water or proton transport within the transmembrane proteins, such as aquaporin, gramicidin and bacteriorhodosin, where water and membrane–wall interactions are expected to be weak [7–9].

The MD simulations for water in (9,9) SWNT of smaller diameter (~12.5 Å) suggest a nanotube-water structure having only the shell water, hence this nanotube-water does not show the pliable water dynamics, although no experimental investigation has yet been conducted. Thus the dynamics of quasi-one-dimensional nanotube-water is very sensitive to the size of the confinement: changing the carbon nanotube radius by a few tenths of an angstrom is enough to switch on and off the channeling of water molecules along the nanotube center. This is of particular relevance to our understanding of the behavior of aquaporin water channels across cell membranes.

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